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An optimised sequential extraction scheme for the evaluation of vanadium mobility in soils

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ABSTRACT

Reviewing the current state of knowledge about sequential extraction applied for soil vanadium (V) fractionation, we identified an urgent requirement of an sequential extraction (SE) specified for V. Namely, almost all previous SE extracted only 8.4%–48% of total V in soils (excluding residue). Thus, we proposed an eight-step SE for V fractionation in soils according to the knowledge gained from literature and our own dissolution experiments with model minerals. After extracting the mobilisable and adsorbed V with de-ionised water and 5 mmol/L phosphate, 1 mol/L pyrophosphate was applied to gather organic matter bound V which minimised the artefact dissolving Al and Fe (hydr)oxides occurred when using HNO_3–H_2O_2 for extraction. Extraction with 0.4 mol/L $NH_2OH \cdot HCl$ was highly selective toward manganese oxides. Fractionation of different crystalline Al and Fe (hydr)oxides associated V with 1 mol/L HCl, 0.2 mol/L oxalate buffer and 4 mol/L HCl at 95°C especially improved the extractability of V incorporated with crystalline phase associated V. The suitability of our new SE scheme was confirmed by its higher selectivity against the target phases and higher extraction efficiencies (55%–77% of total V) with model minerals and 6 soils of different properties than previous SE.

Introduction

Vanadium (V) is a bright white ductile metal belonging to group V in the element periodic table (WHO, 2000). The global average concentration of V is 150 mg/kg in the earth's crust (Byerrum et al., 1974). Its concentration in soils varies depending on the geogenic enrichment and anthropogenic activities (*e.g.*, mining and industrial activities) (Reimann and Caritat, 1998; Teng et al., 2011a). In trace amounts, V is an essential element for normal cell growth (Pyrzyńska and Wierzbicki, 2004). However, V might represent also a hazardous pollutant of the same class of mercury, lead and arsenic (Lazaridis et al., 2003). As such, V has been listed on the United States Environment Protection Agency candidate contaminant list 2 (CCL2). Furthermore, there are an increasing number of people affected by V pollution, especially in USA, China, Russia, and South Africa (Gummow, 2005; Teng et al., 2006; Yang et al., 2014).

The environmental risks of metal(loid)s in soils are primarily decided by their bioavailability and mobility, which depend on the binding state (Stalikas et al., 1999; Bacon and Davidson, 2008; Pueyo et al., 2008; Shaheen and Rinklebe, 2014). Analytical techniques such as X-ray absorption spectroscopy, X-ray diffraction, electron probe micro-analysis, energy-dispersive X-ray spectroscopy, laser-induced breakdown spectroscopy and laser ablation-ICP-MS may be applied to investigate the association of metal(loid)s with different soil solid phases (Keon et al., 2001; Gao, 2007; Rao et al., 2008; Thieme et al., 2010; Jantzi and Almirall, 2014; Cerqueira et al.,

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Table 1 – Summary of the sequential extraction procedures used for the fractionation of V in mineral soils in the literature.

Soil sample	Target fraction	Extraction solution	Averaged percentage of each fraction (%)
(Modified) BCR			
Soils in smelting, mining and agricultural areas and urban parks in China, V_{total}: 71.7–938 mg/kg (n = 55) (Teng et al., 2011a).	Acid soluble	0.11 mol/L HOAc	0.11
	Reducible	0.5 mol/L $NH_2OH{\cdot}HCl$	4.96
	Oxidisable	8.8 mol/L H_2O_2, 1 mol/L NH_4OAc	9.06
	Residual	$HCl–HNO_3$	**84.9**[a]
Surface soils collected at industrial and agricultural sites in Pakistan, V_{total}: 18–108 mg/kg (n = 4) (Khan et al., 2013)	Exchangeable and acid soluble	0.11 mol/L HOAc	1.90
	Reducible	0.5 mol/L $NH_2OH{\cdot}HCl$	12.1
	Oxidisable	30% mol/L H_2O_2, 1 mol/L NH_4OAc	5.58
	Residual	$HNO_3–HF–H_2SO_4–H_2O_2$ or $HNO_3–HF–H_2SO_4–HClO_4$	**74.5**
Industrial soils polluted with V in Italy, V_{total}: 1668 mg/kg with the predominance of V(V) (n = 1) (Terzano et al., 2007)	Exchangeable and acid soluble	0.11 mol/L HOAc	1
	Reducible	0.5 mol/L $NH_2OH{\cdot}HCl$	40
	Oxidisable	30% H_2O_2	16
	Residual	*Aqua regia*	**43**
Soils collected at an industrial sites in England, V_{total}: 85–250 mg/kg (n = 5) (Davidson et al., 1998)	Acid soluble/exchangeable	0.11 mol/L HOAc	0.98
	Reducible	0.1 mol/L $NH_2OH{\cdot}HCl$	12.0
	Oxidisable	8.8 mol/L H_2O_2, 1 mol/L NH_4OAc	16.0
	Residual	*Aqua regia*	**71.0**
Reference soil materials, V_{total}: 87.5–98.3 mg/kg (n = 3) (Žemberyová et al., 2007)	Carbonate, exchangeable	0.11 mol/L HOAc	0
	Iron/manganese oxyhydroxides	0.5 mol/L $NH_2OH{\cdot}HCl$	4.82
	Organic matter and sulfide	8.8 mol/L H_2O_2, 1 mol/L NH_4OAc	3.56
	Residual	*Aqua regia*	**91.6**
(Modified) Tessier et al. (1979)			
An agricultural soil in the vicinity of a V-Ti magnetite mining site in China, V_{total}: 71.8 mg/kg (n = 1) (Yang et al., 2014)	Exchangeable	1 mol/L $MgCl_2$	0
	Carbonates	1 mol/L HOAc/NaOAc	0.14
	Fe and Mn oxides	0.04 mol/L $NH_2OH{\cdot}HCl$ in 25% HOAc	6.96
	Organic matter	0.02 mol/L $HNO_3–H_2O_2$, 3.2 mol/L NH_4OAc in 20% HNO_3	13.2
	Residual	$HCl–HNO_3$	**79.7**
Soils contaminated with industrial wastes in Italy, V_{total}: 35.5–68.4 mg/kg (n = 21) (Abollino et al., 2006)	Exchangeable	1 mol/L $MgCl_2$	0.63
	Carbonates	1 mol/L HOAc, NaOAc	1.25
	Fe and Mn oxides	0.04 mol/L $NH_2OH{\cdot}HCl$ in 25% HOAc	14.0
	Organic matter	0.02 mol/L $HNO_3–H_2O_2$, 3.2 mol/L NH_4OAc in 20% HNO_3	2.48
	Residual	*Aqua regia*–HF, H_3BO_3	**79.5**
Soils from Spain externally spiked with V, V_{total}: 472–2274 mg/kg (n = 5) (Castillo-Carrión et al., 2007)	Soluble	Distilled water	0.28
	Exchangeable	1 mol/L $MgCl_2$	0.12
	Carbonates	1 mol/L HOAc, NaOAc	1.96
	Fe and Mn oxides	0.04 mol/L $NH_2OH{\cdot}HCl$ in 25% HOAc	**64.0**
	Organic matter	0.02 mol/L $HNO_3–H_2O_2$, 3.2 mol/L NH_4OAc in 20% HNO_3	7.18
	Residual	HF–$HClO_4$ mixture	26.6
Soils and sediments influenced by hurricane Katrina in USA, V_{total}: 18.4–126 mg/kg (n = 51) (Shi et al., 2010)	Exchangeable	1 mol/L $MgCl_2$	0
	Carbonates	1 mol/L HOAc, NaOAc	0
	Fe and Mn oxides	0.04 mol/L $NH_2OH{\cdot}HCl$ in 25% HOAc	18.0
	Organic matter	0.02 mol/L $HNO_3–H_2O_2$, 3.2 mol/L NH_4OAc in 20% HNO_3	8.12
	Residual	HF–$HClO_4$ mixture	**73.8**
Soil reference materials, V_{total}: 28.4–109 mg/kg (n = 7) (Li et al., 1995)	Exchangeable	0.5 mol/L $MgCl_2$	0.19
	Carbonates and specifically adsorbed	1 mol/L HOAc, NaOAc	0.91
	Fe and Mn oxides	0.04 mol/L $NH_2OH{\cdot}HCl$ in 25% HOAc	11.3
	Organic matter	0.02 mol/L $HNO_3–H_2O_2$, 3.2 mol/L NH_4OAc in 20% HNO_3	6.85
	Residual	$HNO_3–HF–HClO_4$	**81.3**

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Table 1 (*continued*)

Soil sample	Target fraction	Extraction solution	Averaged percentage of each fraction (%)
Industrial and agricultural soils in Turkey, V_{total}: 17.9–36.6 mg/kg (n = 30) (Güler et al., 2010)	Exchangeable	0.5 mol/L $MgCl_2$	1.11
	Carbonates	1 mol/L HOAc, NaOAc	2.22
	Fe and Mn oxides	0.1 mol/L $NH_2OH{\cdot}HCl$ in HOAc	22.4
	Organic matter	0.02 mol/L HNO_3– 15% H_2O_2	22.4
	Residual	*Aqua regia*	**51.8**
Soils in Poland, V_{total}: 5.58–10.9 mg/kg (n = 7) (Agnieszka and Barbara, 2012)	Exchangeable	0.1 mol/L $MgCl_2$	1.76
	Carbonates	1 mol/L HOAc, NaOAc	1.97
	Fe and Mn oxides	0.04 mol/L $NH_2OH{\cdot}HCl$ in 25% HOAc	38.4
	Organic matter	0.02 mol/L HNO_3–H_2O_2, 3.2 mol/L NH_4OAc in 20% HNO_3	18.3
	Residual	HCl-HNO_3	**39.5**
Other SE methods			
An agricultural soil in the vicinity of a V-Ti magnetite mining site in China, V_{total}: 71.8 mg/kg (n = 1) (Yang et al., 2014)	Non-specifically sorbed	0.05 mol/L $(NH_4)_2SO_4$	0.51
	Specifically sorbed	0.05 mol/L $NH_4H_2PO_4$	0.30
	Amorphous hydrous Fe and Al oxides	0.2 mol/L NH_4^+-oxalate buffer	5.52
	Crystalline hydrous Fe and Al oxides	0.2 mol/L NH_4^+-oxalate buffer +ascorbic acid	9.83
	Residual	HCl–HNO_3	**83.8**
Soil reference materials V_{total}: 36–140 mg/kg (n = 7) (Hall et al., 1996)	Adsorbed, exchangeable and carbonate	1 mol/L NaOAc	0
	Amorphous iron oxyhydroxide	0.25 mol/L $NH_2OH{\cdot}HCl$ in 0.05 mol/L HCl	14.8
	Crystalline iron oxides	1 mol/L $NH_2OH{\cdot}HCl$ in 25% HOAc	24.7
	Organics and sulfide	$KClO_3$–HCl, HNO_3	8.46
	Residual	HF–$HClO_4$–HNO_3	**52.9**
Soils irrigated with waste water in Ethiopia, V_{total}: 9.22–87.4 mg/kg (n = 4) (Fitamo et al., 2007)	Exchangeable	1 mol/L NH_4NO_3	0.07
	Carbonates	0.5 mol/L NH_4OAc, 0.02 mol/L EDTA	14.4
	Reducible	0.175 mol/L NH_4^+-oxalate buffer/0.1 mol/L oxalic acid	**44.8**
	Oxidisable	0.1 mol/L $Na_4P_2O_7$	Not determined
	Residual	7 mol/L HNO_3	40.5

n: number of soils investigated.
BCR: Community Bureau of Reference.
EDTA: ethylenediaminetetraacetic acid.
[a] Bold highlights the prevalent fraction.

2015). They all showed limitations such as difficulties with data analysis of natural samples with high heterogeneity, problems with the separation of the mineral phases from the organic matters in organic soils and limited accessibility (Keon et al., 2001; Bacon and Davidson, 2008). Especially for X-ray absorption spectroscopy, the natural abundance of Ti in soils largely interfering the extended X-ray absorption fine structure detection of V since Ti K-edge (4966 eV) is very close to V K-L3 (4953 eV). Some techniques are less suitable for quantify defined pools of metal(loid)s associated with defined solid phases in soils and sediments, *e.g.*, X-ray diffraction energy-dispersive X-ray spectroscopy. In comparison, sequential extraction (SE) methods cannot only reveal the association of metal(loid)s with soil solid phases but also quantify the pool at mg/kg level. Despite the offset of artefacts during extraction (Rauret et al., 1999; Bacon and Davidson, 2008; Hass and Fine, 2010; Okoro et al., 2012; Drahota et al., 2014), SE may deliver useful information concerning the potentials of metal(loid)s releases from soils and sediments according to the dissolution behaviour of target phases (Keon et al., 2001; Rinklebe and Shaheen, 2014). Especially, SE was evidenced being more powerful to quantify the labile fractions than X-ray absorption spectroscopy (XAS) (Scheinost et al., 2002). Sequential extraction is still very popular today due to its low costs and high accessibility as compared to the other analytical methods for solid phases. In 2014 and 2015, there are still a number of new SE schemes for trace elements that were proposed (Al-Hwaiti et al., 2014; Drahota et al., 2014; Rinklebe and Shaheen, 2014; Shaheen and Rinklebe, 2014; Unsal et al., 2014; He et al., 2015).

To date, Community Bureau of Reference (BCR) scheme is the most popular SE procedure (Ure et al., 1993; Tessier et al., 1979). Some other SE schemes are also available with various combinations of extraction steps and sequences (Wang et al., 1999; Wenzel et al., 2001; Rao et al., 2008; Chang et al., 2009; Huang and Kretzschmar, 2010; Teng et al., 2011a; Aydin et al.,

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2012; Shaheen and Rinklebe, 2014). Since the first SE scheme was developed in late 1970s, there are already numerous SE schemes being proposed (Bacon and Davidson, 2008; Rao et al., 2008; Hass and Fine, 2010; Zimmerman and Weindorf, 2010; Okoro et al., 2012; Shaheen and Rinklebe, 2014), which first focusing on cadmium, chromium, copper, iron, lead, manganese, nickel and zinc, and thereafter on arsenic, mercury, selenium and radionuclides (Bacon and Davidson, 2008; Pueyo et al., 2008; Hass and Fine, 2010; Okoro et al., 2012). However, none of them was designed for the fractionation of V in soils. Khan et al. (2013) presented the only one study with major focus on SE of V in soils. Nevertheless, they aimed at shortening the extraction time of BCR scheme instead improving the extraction recovery. With the representative SE schemes, the previous studies reported surprisingly 70%–90% of total soil V in the residual phases (Table 1). Vanadium geochemistry is very different from the other metal(loid)s. Unlike most other metal(loid)s exiting mostly as either cation or anion in soils, V may present as both cation ($H_2VO_4^-$, HVO_4^{2-}) and anion (VO_2^+, VO^{2+}) (Yang et al., 2010). As a result, a specific SE scheme is needed for soil V to estimate its association with different solid phases in soils.

The industrial demand of V increased drastically currently with tripled global V demand in 2016 than 2002 being predicted (Perles, 2012). The mining and refinery activities may distribute V in the soil environment (Yang et al., 2014). These altogether suggest increased risks of V pollution in soils, which may subsequently affect the human health. Thus, a SE scheme specified for evaluation of V mobility becomes indispensable. Overall, the objectives of this study were (1) to review the current state of knowledge about SE schemes used for V fractionation in soils and to highlight the urgent requirement of a SE scheme for V and (2) to propose a specific SE scheme for V based on the existing literature and on our own preliminary extraction experiments.

1. Materials and methods

1.1. Soil sampling

A permanently anoxic wetland soil (mineral subsoil, 50–60 cm) and a well-drained forest soil (subsoil, 12–30 cm) were sampled in northeast Bavaria, Germany (Huang and Matzner, 2007). A paddy soil (surface soil, 30–35 cm) was sampled in Munshiganj district, 30 km south of Dhaka, Bangladesh (Huang and Kretzschmar, 2010). A mining (topsoil, 0–20 cm) and two smelter soils (topsoil, 0–20 cm and subsoil, 20–40 cm) were collected in Panzhihua, SW-China, which is famous worldwide for mining and smelting V-Ti magnetite (Teng et al., 2011a). All soil samples were homogeneously mixed with at least three random samples from each sample site. After being either freeze- or air-dried and sieved to 2 mm, soil samples were stored at 4°C before use. The characteristics of the aforementioned soils are shown in Table 2.

1.2. Reagents and instruments

All reagents used in this study were of analytical grade and diluted to the required concentration with de-ionised water. All glassware was previously soaked in 14% HNO_3 (V/V) and rinsed with de-ionised water before use. The analysis of V and Fe in extractants was performed with ICP-MS (Agilent 7500ce, Japan) by monitoring ^{51}V and using He collision cell to eliminate the ClO^+ interference (D'Ilio et al., 2011; Rousis et al., 2014) and ICP-OES (Vista-Pro radial, Varian, Germany). Total V in soils were quantified with X-ray fluorescence spectrometry (XRF, Spectro-X-Lab 2000, Germany).

1.3. Sequential extraction procedures

Table 3 summarises our newly proposed eight-step SE scheme (SE I) and a second SE scheme (SE II) modified from the schemes of BCR (Davidson et al., 1998), Tessier et al. (1979) and Wenzel et al. (2001), including the information of target phases and extraction conditions. All SE was conducted with 1.0 g dry soil in a 50-mL centrifugation tube by shaking horizontally at 200 r/min. After each extraction step, the tube was centrifuged for 15 min at 5000 ×*g* and decanted. The remaining solids were twice washed with 8 mL de-ionised water and the residue was taken for the subsequent extraction step. The final residue was additionally digested with HNO_3–H_2O_2–HF (5:3:2, V/V/V) with the assistance of microwave. The supernatant of each extraction step was filtered to 0.45 μm with cellulose acetate and nylon filter papers and stored in polyethylene bottles at 4°C before analysis with ICP-MS.

We evaluated the selectivity of each extraction step by comparing the solubility of synthesised minerals such as ferrous sulfide (FeS; Fluka, Buchs, Switzerland), manganese oxide (MnO_2, pyrolusite) and aluminum hydroxide ($Al(OH)_3$; both Merck, Darmstadt, Germany), boehmite (γ-AlOOH; Sasol, Houston, USA), freshly-prepared 2-line ferrihydrite and goethite (α-FeOOH) at 4 and 8 g/L during each extraction step. Based on X-ray diffraction analysis, ferrihydrite and γ-AlOOH were poorly crystalline and FeS, MnO_2, $Al(OH)_3$, and α-FeOOH were well-crystalline phases. Furthermore, we validated the

Table 2 – Characterisations of the soils used in this study.

Parameter	Mining soil	Forest soil	Smelter topsoil	Smelter subsoil	Wetland soil	Paddy soil
pH	7.60	3.49	8.00	8.32	4.70	6.95
Organic C (%)	2.15	8.27	10.9	2.58	5.56	2.90
V (mg/kg)	343	48.8	784	150	23.5	111
Fe (%)	11.1	1.69	24.0	5.04	1.09	4.31
Mn (%)	0.15	0.01	0.23	0.66	0.02	0.05
Al (%)	3.14	5.15	2.73	4.31	5.66	6.42
Si (%)	10.0	23.6	8.56	13.1	22.4	23.2

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Table 3 – Sequential extraction procedures for V fractionation in mineral soils proposed in this study.

Target fraction	Operation condition	Extraction condition
SE I		
1 Water-soluble	15 mL de-ionised water	RT, 6 hr
2 Strongly adsorbed	25 mL of 5 mmol/L phosphate ($NH_4H_2PO_4$), pH 4.5	RT, 8 hr
3 Organic matter	25 mL of 0.1 mol/L pyrophosphate ($Na_4P_2O_7{\cdot}10H_2O$)	RT, 4 hr
4 Mn oxides	25 mL of 0.4 mol/L $NH_2OH{\cdot}HCl$, pH 3.2	RT, 2 hr
5 Very poorly crystalline Fe and Al (hydr)oxides	25 mL of 1 mol/L HCl	RT, 4 hr, 1 repetition
6 Poorly crystalline Fe and Al (hydr)oxides	25 mL of 0.2 mol/L NH_4-oxalate buffer (pH 3.25)	RT, 4 hr in the dark, 1 repetition
7 Crystalline Fe and Al (hydr)oxides	25 mL of 4 mol/L HCl	95°C, 3 hr, agitation twice per hr
8 Residual	10 mL of HNO_3–H_2O_2–HF (5:3:2, V/V/V)	Microwave digest: 150°C, 10 min, 190°C, 20 min, 100°C 20 min
SE II		
1 Water-soluble	15 mL de-ionised water	RT, 6 hr
2 Exchangeable	25 mL of 1 mol/L HOAc	RT, 8 hr
3 Amorphous Fe and Al (hydr)oxides	25 mL of 0.2 mol/L NH_4-oxalate buffer, pH 3.25	20°C, 4 hr, in the dark
4 Crystalline Fe and Al (hydr)oxides	25 mL of 0.2 mol/L NH_4-oxalate buffer + 0.1 mol/L ascorbic acid, pH 3.25	(96 ± 3)°C, 30 min, occasional agitation
5 Organic matter	0.02 mol/L HNO_3 + 30% H_2O_2 (W/W), 3.2 mol/L NH_4OAc in 2 0% (V/V) HNO_3	(85 ± 2)°C, 5.5 hr, occasional agitation
6 Residual	10 mL HNO_3–H_2O_2–HF (5:3:2, V/V/V)	Microwave digest: 150°C, 10 min, 190°C, 20 min, 100°C 20 min

RT: room temperature, (25 ± 2)°C.

proposed scheme by examining whether the results obtained from the SE matched with the characteristics of the forest, wetland, mining, smelter and paddy soils (Table 2). To check the correctness of V mass balance, the sum of V concentrations from each extraction step including the residue was compared with the total V concentrations in soils measured with XRF. The method precision of each extraction step was evaluated by the coefficient of variation of each fraction with SPSS 20.

2. Results and discussion

2.1. *Sequential extraction for vanadium in mineral soils in literature*

Table 1 summarised all SE schemes used to fractionate V in soils to date. The most commonly used scheme was exchangeable (sorbed)/carbonate/reducible (or Fe and Mn (hydr)oxides)/oxidisable (or organic matter and sulfides) fractions. Wenzel et al. (2002) and Hall et al. (1996) additionally separated Fe and Al (hydr)oxide phases into two fractions based on the crystallinity. Generally, the extractant used for mobilisable fractions was water, neutral salt or weak acid which is well-accepted. Almost all studies showed that less than 1% of total V in soils was exchangeable (Table 1), suggesting the general low mobility of V in soils (Hall et al., 1996). In most cases, hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) was applied to extract reducible phases/Fe and Mn (hydr)oxides and extracted less than 12% of total V in soils (Table 1). The oxidisible V was usually extracted by H_2O_2 and a proportion of <16% of total V has been found among the different soils. Since oxidation may also release organic matter bound V, oxidation reagents such as $KClO_3$–HCl and HNO_3 were proposed also to digest the organic matter associated phases (Hall et al., 1996). The predominance of V in reducible phases/Fe and Mn (hydr)oxides (45%–64%) was only found in those soils with external V origin *e.g. via* experimentally spiking (Castillo-Carrión et al., 2007) or irrigation of waste water (Fitamo et al., 2007). This mirrored that added V, mostly V(V), was predominately associated with Fe/Mn (hydr)oxides due to its strong adsorption affinity (Peacock and Sherman, 2004). Most SE schemes in literature allowed extract 10%–30% of total V in natural soils, when excluding the residue. Such low extraction efficiencies may reflect the incorporation of V into the lattice crystalline minerals as tetravalent (V(IV)) and trivalent V (V(III)) cations (*e.g.* VO^{2+} and V^{3+}) (Gehring et al., 1993; Klein et al., 1993; Schwertmann and Pfab, 1994). These altogether suggest the current SE methods in literature being still unsuitable for fractionation of V in soils, especially when V is associated with recalcitrant phases.

2.2. *Development of new sequential extraction schemes for vanadium in soils*

For safety reason, we avoided using very strong oxidants, acids and toxic reagents to propose our novel SE scheme (SE I). First, we extracted the soil with de-ionised water to quantify the pool of readily mobilisable V. Namely, the water soluble phase constitutes the most mobile and potentially the most available metal(loid)s. Then, because the mobile V in soils is mostly pentavalent (V(V)) (Baken et al., 2012), phosphate solution was used for exchange strongly adsorbed V *via* competitive adsorption due to the similarity of the chemical structure between phosphate and vanadate (Prathap and Namasivayam, 2010). Phosphate may outperform vanadate because of its smaller size and higher charge density (Lookman et al., 1995; Rietra et al., 1999; Wenzel et al., 2001). We decreased phosphate concentrations to 5 mmol/L and shortened the extraction time to 8 hr,

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which successfully extracted more than 80% of exchangeable arsenic in soils (Huang and Kretzschmar, 2010), as compared Wenzel et al. (2001). The use of lower phosphate concentration and shortage of the extraction duration may minimise to extract organic matter associated V. Namely, phosphate is capable of complexation with polyvalent cations, *e.g.*, Ca^{2+}, Al^{3+} and Fe^{3+}, which are responsible for maintaining organic matter in a flocculated and insoluble state in soils, however weaker than pyrophosphate (Lente et al., 2000). Both acetic acid (HOAc) and ethylenediaminetetraacetic acid (EDTA) were also common reagents for quantifying mobilisable and bioavailable metal(-loid)s (Teng et al., 2011b; Tian et al., 2014). However, HOAc was insufficient to release the adsorbed vanadate since it only slightly lowered the pH and almost did not change the adsorption affinity of vanadate to soil particles (Tian et al., 2014). Wenzel et al. (2001) found that EDTA was not selective enough because it may dissolve considerable amounts of Fe and Al (hydr)oxides. Following phosphate extraction, we used pyrophosphate to destabilise the soil organic matter in complex with polyvalent cations and released V associated. Pyrophosphate is commonly used to extract metal(loid)s bound to organic matters and to avoid the dissolution of metal oxides (Huang and Kretzschmar, 2010). Since pyrophosphate may also exchange adsorbed vanadate from soils, phosphate extraction was done prior to pyrophosphate extraction. The dissolution test with different model minerals showed that none of the model minerals could be dissolved by 5 mmol/L phosphate and about 1% of boehmite and FeS was dissolved during pyrophosphate extraction (Table 4), highlighting also the much stronger ability of pyrophosphate to complex metals than phosphate. The design of our extraction sequence allowed us conclude that the amount of organic matter associated V extracted by 5 mmol/L phosphate was trivial as compared to 0.1 mol/L pyrophosphate. Still, future research is essential to quantify how good the two phosphate extractions differentiate adsorbed and organic matter associated V.

To extract V associated with Fe and Al (hydr)oxides in soils, most methods in literature used $NH_2OH{\cdot}HCl$ alone or in combination with HCl or HOAc at high temperatures (Table 1). However, $NH_2OH{\cdot}HCl$ has been found inefficient to dissolve amorphous ferrihydrite in the given time, whereas our preliminary experiments indicated complete dissolution of Mn oxides in 30 min with 0.4 mol/L $NH_2OH{\cdot}HCl$ (Table 4). Dissolution of boehmite and FeS were <1.5% and <0.15% for ferrihydrite and goethite, showing the high dissolution selectivity of 0.4 mol/L $NH_2OH{\cdot}HCl$ toward MnO_2. Hence we utilised $NH_2OH{\cdot}HCl$ to quantify Mn oxide instead of Fe and Al (hydr)oxide bound V. Given that V(III) and V(IV) may incorporate into the lattice of soil minerals of different crystallinity, we refined the fraction associated with Fe and Al (hydr)oxides by separating it into very poorly crystalline, poorly crystalline and crystalline. The corresponding extraction reagents were 1 mol/L HCl, 0.25 mol/L oxalate buffer and 4 mol/L hot HCl, respectively. The extraction sequence using 1 mol/L HCl and 0.25 mol/L oxalate buffer was adapted from Keon et al. (2001) and higher HCl concentrations or hot HCl should be avoided to minimise ligand-promoted dissolution of crystalline Fe (hydr)oxides (Huang and Kretzschmar, 2010). Our dissolution test showed complete dissolution of poorly crystalline ferrihydrite and 6.3% of poorly crystalline boehmite using 1 mol/L HCl (Table 4). The percentage of crystalline goethite and $Al(OH)_3$ dissolved were comparably low (3.9% and 1.2%, respectively). Thus, the extraction based on 1 mol/L HCl was especially selective toward poorly crystalline Fe (hydr)oxides. The dissolution ability of oxalate buffer was generally similar to 1 mol/L HCl but may dissolve more poorly crystalline boehmite (10.9%) than 1 mol/L HCl (Table 4). Dissolution of the crystalline phases is the most challenging for SE. Using *aqua regia* and strong oxidant acids, which were frequently taken for dissolution of the residual phase (Table 1), may risk to dissolve partially silicate (Yuan et al., 2004; Silveira et al., 2006; Rao et al., 2011). Cornell and Schwertmann (2003) suggest to dissolve crystalline Fe (hydr)oxide with 6 mol/L HCl at room temperature. However, our preliminary study showed slight dissolution of goethite and the dissolution of boehmite was less effective (Table 4). Increasing temperature to 95°C, complete dissolution of goethite and boehmite was achieved with 4 mol/L HCl in 1 hr and therefore was used in our SE scheme to extract crystalline Fe and Al (hydr)oxide associated V. Reduced minerals such as sulfides may be present in anoxic and redox fluctuated soils such as wetland, flooded and paddy soils. Our extraction steps used for Fe and Al (hydr)oxides may also extract amorphous

Table 4 – Dissolution efficiencies of extraction procedures proposed in this study toward Fe and Al minerals of different crystallinity.

Extractant[a]	Ferrihydrite	Goethite	Boehmite	$Al(OH)_3$	MnO_2	FeS
	Poorly crystalline	Well-crystalline	Poorly crystalline	Well-crystalline	Well-crystalline	Well-crystalline
	Dissolution efficiency (%)					
Phosphate (5 mmol/L)	0	0	0	0	0	0
Pyrophosphate (0.1 mol/L)	0.05 ± 0.01[b]	0.54 ± 0.04	1.27 ± 0.09	0.29 ± 0.01	0.03 ± 0.01	1.16 ± 0.01
$NH_2OH{\cdot}HCl$ (0.4 mol/L)	0.11 ± 0.01	0.09 ± 0.01	0.95 ± 0.24	0.07 ± 0.01	99.7 ± 2.96	1.27 ± 0.04
HCl (1 mol/L)	95.6 ± 4.21	3.94 ± 0.10	6.31 ± 0.43	1.18 ± 0.02	0.10 ± 0.01	17.5 ± 0.17
Oxalate buffer (0.2 mol/L)	71.5 ± 3.15	4.61 ± 0.07	10.9 ± 0.90	0.40 ± 0.01	37.2 ± 1.13	6.06 ± 0.91
HCl (4 mol/L, 95°C)	98.7 ± 1.88	98.9 ± 1.62	95.4 ± 1.90	100 ± 1.49	52.1 ± 0.42	64.1 ± 0.95

[a] Detailed dissolution conditions are shown in Table 3.
[b] Mean ± standard deviation.

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sulfides, *i.e.*, 1 mol/L HCl may extract acid volatile sulfide and 4 mol/L hot HCl was evidenced to dissolved 64.1% of well-crystalline FeS.

We proposed a second SE scheme (SE II) for V fractionation in mineral soils by combining steps from the most frequently used schemes of Tessier et al. (1979), BCR (Davidson et al., 1998) and Wenzel et al. (2001). Sequential extraction II served as a comparison of the effectiveness and feasibility for our newly proposed eight-step SE scheme (SE I) (Table 3). We added de-ionised water extraction as first step to quantify the readily mobilisable V. Acetic acid was chosen to extract exchangeable V by lowering pH and additionally to extract carbonate phases (Tessier et al., 1979; Davidson et al., 1998). Iron and Al (hydr)oxides fraction was categorised into amorphous and crystalline phases based on Wenzel et al. (2001) using oxalate buffer in combination with ascorbic acid. Subsequently, HNO_3–H_2O_2 based extraction was applied to decompose organic matters (Tessier et al., 1979).

2.3. *Comparison of the selected schemes of sequential extraction*

To verify the suitability of the eight-step SE scheme (SE I), we first compared its results on two soil samples of very different characteristics with those obtained with SE II scheme (Fig. 1). The mining soil is slightly basic (pH 7.6) and enriched with geogenic V (Yang et al., 2014). The forest soil is acidic (pH 3.5) and developed from granite enriched with Fe and Al oxides and organic matter due to podsolisation (Huang et al., 2004). The comparison demonstrated that 5 mmol/L phosphate released strongly adsorbed V more efficiently (*e.g.*, 3.9% in the forest soil) than 1 mol/L HOAc solution (*e.g.*, 2.2% in the forest soil). Namely, the pH in the HOAc extracts of both soils was measured as 4, which was insufficient to weaken the adsorption affinity of vanadate (Peacock and Sherman, 2004). The proportion of V bound to organic matter in the forest soil was higher based on pyrophosphate extraction (9.8%) than that based on HNO_3–H_2O_2 extraction (8.7%). Pyrophosphate dissolves organic matter from soils by forming metal complexes, whereas HNO_3–H_2O_2 extracts organic matter bound metal(loid)s by oxidising organic matter to CO_2. The forest soil was collected from a Bhs horizon of a podzol soil profile enriched with organic substances (8.27% organic carbon) precipitated from the forest floor. Thus, a high percentage of organic matter bound V can be expected. The mining soil contained less organic carbon (2.15%). Still, a similarly higher percentage of organic bound V (5.9%) in the mining soil to that in the forest soil was found based on HNO_3–H_2O_2 extraction. In comparison, pyrophosphate measured only 0.3% of total V associated with organic matter in the mining soil. Apparently, H_2O_2–HNO_3 released additional V *via* the dissolution of considerable amounts of Fe and Al (hydr)oxides, as indicated by higher concentrations of Fe in the H_2O_2–HNO_3 extracts (>56,000 mg/kg) than those in the pyrophosphate extracts (625 mg/kg Fe for mining soil, 2107 mg/kg Fe for forest soil). These results indicated that pyrophosphate may be not only more effective but also more selective against the organic matter bound V than HNO_3–H_2O_2.

The presence of significant amounts of V associated with Mn oxides (9.3%) in the forest soil demonstrated the usefulness of $NH_2OH{\cdot}HCl$ extraction step in SE I (Fig. 1). Overall, SE I quantified more V associated with metal (hydr)oxides in the forest soil (total of 63%) than SE II did (total of 48%). Sequential extraction I measured 16% of total V associated with very poorly and poorly crystalline Fe–Al (hydr)oxides and 37% with crystalline Fe–Al (hydr)oxides in the forest soil. Based on SE II, there were only 20% of total V bound to amorphous (hydr)oxides and 28% bound to crystalline (hydr)oxides. Such difference was much more apparent in the mining soil. There was 14% of total V bound to Mn oxides and poorly crystalline Fe–Al (hydr)oxides, and 43% bound to crystalline Fe–Al (hydr)oxides according to SE I. In comparison, only 1.0% of total V was found in the amorphous oxides fraction and 1.0% in crystalline oxides fraction by SE II.

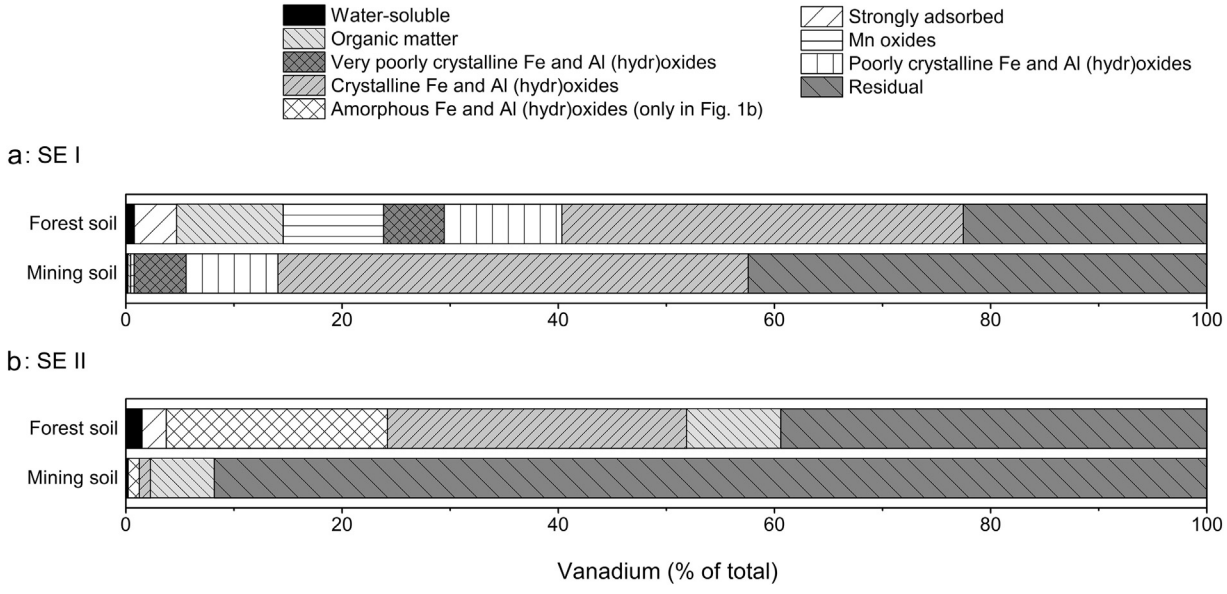

Fig. 1 – Relative distribution of V in different fractions of sequential extraction I (SE I) (a) and sequential extraction II (SE II) (b) in the mining and forest soil. The data was the mean values of three replicates extractions.

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Although the Fe concentration in the mining soil (11.1%) was much higher than in the forest soil (1.69%), SE II measured much less V associated with Fe–Al (hydr)oxides in the mining soil (2.1%) than in the forest soil (48%). This is in disagreement with the positive correlation between Fe and V generally found in soils (Aide, 2005). Of course, such discrepancy can be explained by the abundance of geogenic V associated with more recalcitrant phase, *e.g.*, crystalline V-Ti magnetite in the mining soil. However, SE I largely improved the extraction efficiency of metal oxides bound V in the mining soil so that the ratio of the proportion of metal oxides bound V between both soils was almost 1:1. Thus, SE I was able to refine and target the fractions related to the metal (hydr)oxides with greater efficiency than SE II. Overall, SE I quantified 77% and 58% of total V excepted the residual fraction in the forest soil and mining soil, respectively (Fig. 1). Sequential extraction II, which is a combination of the most commonly used SE schemes, extracted in comparison only 61% and 8% of total V in the forest and mining soils, respectively, suggesting that our newly proposed eight-step SE scheme (SE I) largely improved the ability of SE to fractionate V in soils.

2.4. *Verification of the proposed eight-step sequential extraction scheme with real soil samples*

Four further soils of different characteristics at 23.5 to 784 mg/kg V (Table 2) were analysed to check the adaptability and reproducibility of our eight-step SE scheme (SE I) in addition to the selectivity test with model minerals during the development (Section 3.2). When including the results of the mining soil and forest soil, our newly proposed SE scheme is highly superior to the previous schemes by increasing the total extraction recovery from averagely 27% of total V (8.4%–48%) in 192 soils in literature to 65% (55%–77%) in 6 soil samples investigated here when residues not included. Satisfactory V mass balance was shown with averagely 95% of V in soils was quantified with our new SE scheme (including residue) as compared to XRF values. The variation coefficients of each extraction step averaged 3.8%, indicating our extraction method was highly precise (Tables S1 and S2). The low precision was mainly from the water soluble fraction (13%) and residual fraction (19%) due to the very low concentrations in the water extracts and trace amounts of soils left for digestion, respectively.

The proportion of water-soluble fraction of the six soils samples was 0.6% (0.1%–1.1%) and the exchangeable fraction was 1.2% (0.1%–3.9%). The 5 mmol/L phosphate was plausible to effectively release strongly adsorbed V from soils *via* competitive adsorption, which is indicated by the much lower concentrations of V in the phosphate extracts of the different soils investigated (0.15–7.7 μmol/L). Excessive competitive species are known being able to release adsorbed species effectively (Sparks, 2003). In this study, the phosphate concentration used was approximately 3 levels of magnitude higher than adsorbed vanadate in the extracts. The large excess of phosphate warranty also the recovery of adsorbed little influenced by the original soil pH. Independently of the soil characteristics, most V in soils was scarcely mobilisable (Figs. 1 and 2). The very small pool of readily mobilisable V found in these soils is in agreement with the results derived from the soil column leaching experiments (Yang et al., 2014). The fraction associated with organic matters ranged from 0.3% to 24% and was well related with the soil organic carbon contents ($P = 0.02$, excluding the smelter topsoil which was artificially affected). The highest proportions of V associated with organic matter were found in the forest and wetland soils which contain 8.3% and 5.6% organic matter, respectively (Table 2). The proportion of V associated with Mn oxides averaged only 2.6% (0.2%–9.3%), coinciding well with the general low content of Mn oxides in soils compared to Fe and Al (hydr)oxides (Sparks, 2003). In the wetland soil, the proportion of the reducible fraction (*i.e.*, Mn and Fe (hydr)oxides) was much smaller than in the other soils, which is plausible due to its anoxic nature. On average, 34% (28%–43%) of total V was bound to crystalline Fe and Al (hydr)oxides and 9.2% (4.6%–17%) V was associated with poorly crystalline Fe and Al (hydr)oxides. The proportion of very poorly crystalline fraction was 8.6% (1.7%–22%). Vanadium was more strongly associated with the crystalline Fe and Al (hydr)oxides than the amorphous Fe and Al (hydr)oxides, which reflects the incorporation of geogenic V in the lattice of soil minerals as V(III) and

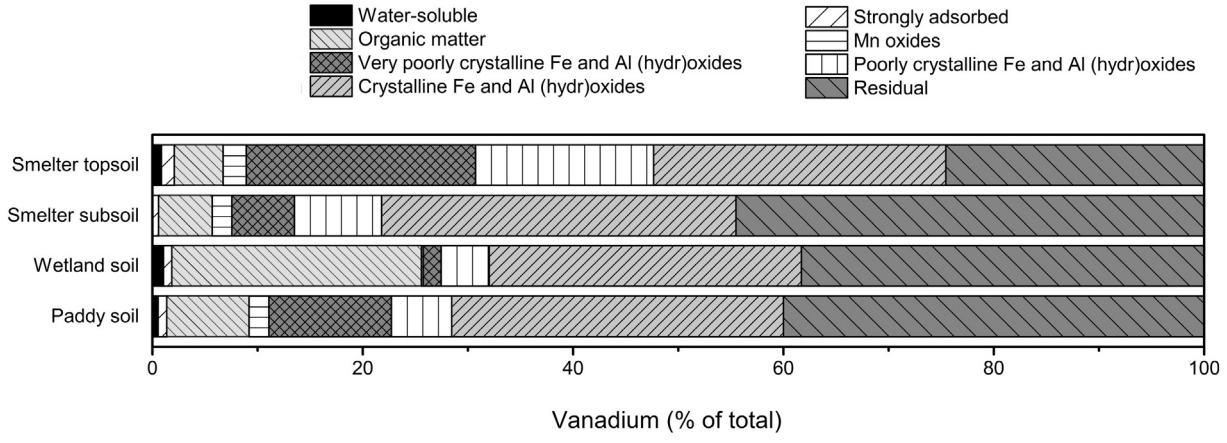

Fig. 2 – Relative distribution of V in different fractions of the proposed eight-step sequential extraction in the smelter, wetland and paddy soils. The data was the mean values of three replicates extractions.

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V(IV) (Gehring et al., 1993; Klein et al., 1993; Schwertmann and Pfab, 1994). In addition, the proportion of V associated with Fe and Al (hydr)oxides increased with the increasing concentrations of total V and Fe in soils, supporting the close correlation between V and Fe in soils (Kaur et al., 2009).

Since our scheme was developed using natural and low contaminated soils, it may not be able to resolve certain V containing wastes such as dicalcium silicate, brownmillerite, hydrogarnet and sodalite/cancrinite (De Windt et al., 2011; Frost and Xi, 2012). Accordingly, care should be taken for applying this scheme to the soils embodying high amounts of V containing wastes.

3. Conclusions

We have demonstrated that our newly-proposed eight-step SE was able to target the distinct and environmentally important forms of V in soils. The new SE scheme efficiently refined the fraction of V bound to Mn, Fe and Al (hydr)oxides, which can be useful for the evaluation of V mobilisation under reducing conditions. The largely improved extractability against crystalline Fe and Al (hydr)oxide enabled for the first time to identify the presence of noticeable amounts of geogenic V incorporated in the lattice of soil minerals. Furthermore, the newly-proposed SE scheme is highly superior to the previous schemes by largely increasing the total extraction efficiency. It extracted averagely 65% (55%–77%) of total V in 6 natural soil samples investigated (residues not included), while the schemes used in literature extracted 27% of total V (8.4%–48%) of total V in 192 natural soil samples.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.jes.2016.02.019.

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